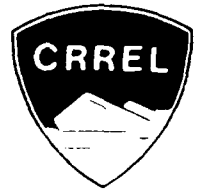CRREL

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PREFACE

This report was prepared by Dr. Harold S. Boyne, Chief, and David J. Fisk, Physical Sciences Technician, both of the Geophysical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided under DA Project 4A762730AT42, *Design, Construction and Operations Technology for Cold Regions*; Task FS, *Fire Support*; Work Unit 012, *Influence of State-of-the-Art Screeners on a Snow Cover*.

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A Laboratory Comparison of Field Techniques for Measurement of the Liquid Water Fraction of Snow

HAROLD S. BOYNE AND DAVID J. FISK

INTRODUCTION

Knowledge of the liquid water content of a snow cover is important in assessing the snow's mechanical strength, and rates of meltwater generation and transmission. It also has a profound effect on the performance of passive and active remote sensing systems operating over snow.

New absolute liquid water measurement methods—alcohol calorimetry (Fisk 1986) and dilution (Davis et al. 1985)—have been developed that compare favorably with freezing calorimetry (Jones et al. 1983). Another development is a capacitance sensor, which offers rapid measurement of liquid water at the surface and with depth, but requires calibration against an absolute method (Ambach and Denoth 1980). Which method one uses depends on factors such as desired sample size, available equipment, experimental design and desired accuracy. Our purpose was to test measurement equivalence and accuracy by comparing the three absolute measurement methods and by comparing the capacitance method with one of the absolute methods. The work was done in a laboratory coldroom where the snow homogeneity and wetness could be controlled.

DESCRIPTION OF EXPERIMENTS

Snow samples were prepared in a 0.5-×0.5-×0.75-m insulated box that had drainage holes drilled into the bottom, and one side that could be removed in sections for access to the snow. With the coldroom at –5 to –10°C, snow was sifted into the box and covered. The coldroom was then warmed to about 3°C and the snow allowed to come to 0°C throughout its volume, determined by inserting calibrated thermometers. After water began to drain from the box, one snow sample was taken for each pair of measurements, mixed to assure uniformity, and divided between the two measurement procedures.

In all of the measurements, the alcohol calorimeter method was used as the transfer standard. That is, alcohol calorimetry was compared to the dilution method; alcohol calorimetry was compared to freezing calorimetry; and alcohol calorimetry was compared to the capacitance method. Each of the measurement techniques is described in detail elsewhere (Jones et al. 1983, Davis et al. 1985, Fisk 1986), so we describe them only briefly.

Alcohol calorimetry

The alcohol calorimeter uses 25 g of snow and 80 g of methanol. Separate ice water baths maintain the calorimeter reaction cup and preweighed methanol at 0°C. The snow sample is placed in the calorimeter, then the methanol is poured in. Figure 1 is a plot of temperature versus time for the snow–methanol mixture, showing the decrease as the ice fraction of the snow dissolves (the liquid water dissolves virtually instantaneously), and then the near linear ($r > 0.99$) increase as the methanol–water mixture warms toward 0°C. The temperature
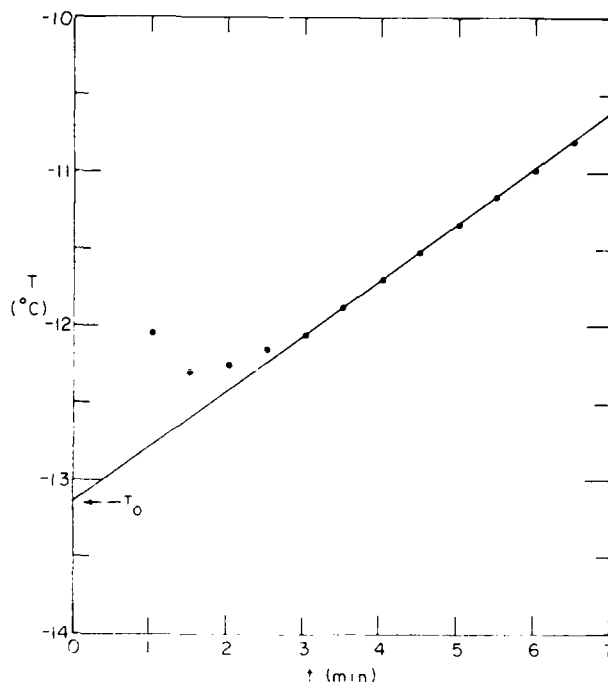
*Figure 1. Alcohol calorimetry: temperature vs time plot
and extrapolation to t = 0, which determines $T_0 = -13.2°C$.*

T_0 at $t = 0$ is obtained by extrapolation from the linear part of the plot. The liquid water fraction by mass for the calorimeter used in this study is

$$L_m = \frac{T_0 - (-16.72°C)}{8.17 - (-16.72°C)} \ g/g = (0.04T_0 + 0.67)g/g$$

where -16.72°C and 8.17°C are the empirically obtained values of T_0 for liquid water fractions of 0 and 1, respectively. Careful calorimeter calibration, preweighing the methanol, maintaining the methanol and calorimeter at 0°C, and keeping the methanol dry with a drying agent are the main requirements for successful measurements.

Freezing calorimetry

Freezing calorimetry has its own special requirements. The freezing agent must be insoluble in water so that no heat is generated by solvent–solute interaction. A commonly used freezing agent is a low-viscosity silicone oil. Unfortunately, the physical properties of silicones often vary between production batches, so the specific heat of a given batch of silicone oil must be determined from –50 to –20°C before it is used for calorimetry. The values given in handbooks or by manufacturers generally are not accurate enough for this application.

The heat gained by the calorimeter during a measurement must also be determined. The heat gained by the calorimeter is

$$EC_f(T_2 - T_1)$$

where F = calorimeter's heat capacity, in terms of mass of the freezing agent
  C_f = freezing agent's specific heat at temperature $(T_1 + T_2)/2$
  T_1 = initial temperature of the freezing agent
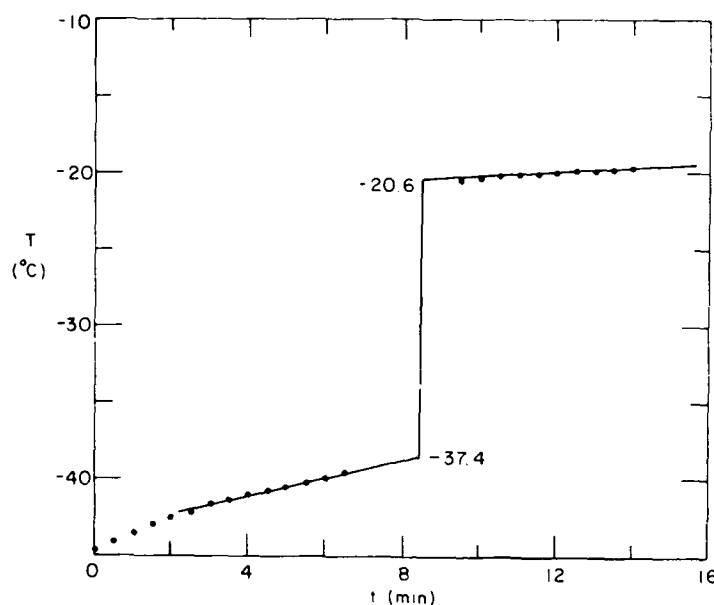 T_2 = final temperature of the snow–freezing agent mixture.

2

Figure 2. Freezing calorimetry: temperature vs time plot before and after snow is added. Extrapolation of $T_1 = -37.4°C$ *and* $T_2 = -20.6°C$ *at 8.25 minutes is shown.*

T_1 and T_2 are determined by extrapolation from plots of temperature versus time, as shown in Figure 2.

In these experiments, E_{meth} was determined using methanol, whose specific heat as a function of temperature is known. Since the heat gain of the calorimeter is independent of the working fluid, $EC_f \Delta T$ is constant and $E_{meth} C_{meth} = E_{si} C_{si}$ for any temperature change ΔT where E_{meth}, E_{si}, C_{meth}, C_{si} are the heat capacities of the calorimeter, in terms of mass of the working fluid, and specific heats for methanol and silicone oil working fluids respectively. From E_{meth}, E_{si} can be calculated and the temperature dependence of C_{si} determined.

The snow sample must be added to the freezing calorimeter in small pieces so that no large frozen chunks result. Large chunks tend to freeze at their surfaces, leaving unfrozen water inside. This, in turn, leads to a systematically low determination of their liquid water content.

Dilution

Dilution measurements require that the insulated container and stock solution be at 0°C to prevent melting or freezing of the snow sample. This is accomplished by placing an ice–water mixture in a plastic bag in the container and by storing the stock solution in an ice–water bath. Measurements of specific conductance must be made with all sample fluids at the same temperature. We used approximately 1 L of snow and enough stock solution to obtain a unity mass ratio of sample to stock solution.

Capacitance meter

The capacitance snow moisture meter has a sensing plate with dimensions of $0.15 \times 15 \times 15$ cm and senses a snow volume of about $4 \times 15 \times 15$ cm, or 900 cm^3. The meter measures the electrical capacitances of the air and snow, then other equipment is used to measure the sensed snow's density. The snow's volumetric liquid water content L_v is calculated from these three data. Dividing by the snow's density ρ_s gives liquid water content by mass. Since 90% of the meter's information comes from within ± 2 cm of the plate, it is important that full contact between the snow and plate be obtained.

3

RESULTS AND ANALYSIS

Table 1 shows the results of the comparisons between alcohol calorimetry and freezing calorimetry, dilution and the capacitance meter. To test the equivalence of the methods, we conducted tests of significance in which the hypotheses are:

$$\mu_F = \mu_A$$
$$\mu_D = \mu_A$$
$$\mu_C = \mu_A$$

where μ_F, μ_D, μ_C and μ_A are the mean values of measurements made by freezing calorimetry, dilution, capacitance meter and alcohol calorimetry respectively (Hoel 1976).

The analysis of the paired comparisons is given in Table 2. The value $F = V_c/V_e$, where V_c is the mean square of the column means and V_e is the mean square of the variation in all measurements (due to measurement errors and spatial variations in liquid water content of the snow). If $F > F_c$, the critical value chosen for the test, then that value of F has a low probability of occurrence, and the hypothesis that $\mu_x = \mu_A$ is rejected.

From the tests of significance we see that $F < F_c$ in all of the comparisons, and it is probable that no bias exists in any of the measurements. We accept the hypotheses that the means of the groups of paired measurements are the same and the measurement methods are equivalent.

The random errors associated with each of the techniques have been discussed in the articles originally describing the methods. By fitting a regression line to the paired values in a given comparison, we can calculate the standard error of estimate s_e. We are 95% confident that all test values will fall within $\pm 1.96\, s_e$ of the regression line. The 95% confidence intervals for the comparisons are given in Table 3.

The absolute errors of the methods have been estimated to be ± 1 to 2 g water/100 g snow for freezing calorimetry, ± 1 g water/100 g snow for the dilution method, and ± 1 g water/100 g snow for the alcohol method. The capacitance meter used in this study was calibrated by comparison with a freezing calorimeter with reported accuracy of 0.5 g water/100 cm³ snow. The meter's accuracy is limited to that of the calibration method. The error in the meter's electronics produces an additional liquid water error of 0.2 to 0.4 g water/100 cm³ snow, depending on snow wetness and density.

The error in measuring snow density ρ with a 200-cm³ cutter type sampler was estimated by measuring the density of dry snow at $-3°C$ with the cutter and with the capacitance meter. The standard error s_e of these measurements was 2 g/100 cm³ snow. This uncertainty could be attributable to the sampling error of the cutter, electronic error in the meter, or variations in snow density between the 200-cm³ volume sampled by the cutter and the 900-cm³ volume sensed by the meter. Of all density measurements, 95% will be in error by less than $1.96\, s_e$ or 4 g/100 g snow. This maximum density error will contribute 0.2 to 0.5 g water/100 cm³ snow error to the capacitance moisture measurement. Thus, the sum of all maximum errors for the dielectric meter is 1.0 to 1.4 g water/100 cm³ snow, with 95% confidence.

The measurement uncertainty for the alcohol calorimeter determination of mass liquid water content is 1 g water/100 g snow, resulting from temperature and weighing errors. Since the 95% confidence interval for snow density measurements is 4 g/100 cm³, the 95% confidence interval for volume liquid water by alcohol calorimetry is

$$\Delta L_v \cong L_m \cdot \Delta\rho + \Delta L_m \cdot \rho$$

$$= \frac{20 \text{ g water}}{100 \text{ g snow}} \cdot \frac{4 \text{ g snow}}{100 \text{ cm}^3 \text{ snow}} + \frac{1 \text{ g water}}{100 \text{ g snow}} \cdot \frac{4 \text{ g snow}}{100 \text{ cm}^3 \text{ snow}}$$

$$= 1.2 \text{ g water/100 cm}^3 \text{ snow, for } \rho = 4 \text{ g/100 cm}^3, \text{ and } L_m = \frac{20 \text{ g}}{100 \text{ g}}$$

4

Table 1. Comparison of laboratory measurements (liquid water percent by mass L_m and by volume L_v) from alcohol calorimetry and other methods (definitions at end of Table 2).

Date	Freezing calorimeter L_m	Alcohol calorimeter L_m	x_i		Date	Dilution L_n	Alcohol calorimeter L_m	x_i		Date	Capacitance meter L_v	Alcohol calorimeter L_v	x_i
20 May 1986	9.5	9.6	9.6		14 May 1986	4.4	5.6	5.0		5 November 85	1.9	2.6	2.2
	11.4	11.6	11.5			9.6	9.1	9.5			1.0	0.6	0.8
	9.9	11.2	10.6			8.0	8.0	8.0			5.7	2.8	3.2
	11.7	12.9	12.3			8.8	8.9	8.8			3.1	3.2	3.2
21 May 1986	8.2	9.2	8.7		15 May 1986	4.3	5.8	5.0		21 January 86	0.3	0.6	0.4
	7.8	9.6	9.7			5.9	7.9	6.9			-0.2	0.2	0.0
	8.3	10.0	9.2			3.4	2.7	3.0			3.3	2.1	2.7
	8.9	10.5	9.7			9.6	9.8	9.7			3.4	3.4	3.4
22 May 1986	7.6	7.1	7.4			6.7	6.3	6.5		22 January 86	4.6	4.7	4.6
	7.2	8.5	7.8			5.7	6.9	6.3			3.8	4.9	4.4
	7.3	8.3	7.8			8.0	5.6	6.8			3.5	2.6	3.0
	10.1	9.7	9.9			6.4	5.4	5.9			2.8	0.2	1.5
	10.8	9.5	10.2			4.7	8.0	6.4			0.9	0.4	0.6
28 May 1986	10.9	8.7	9.8		16 May 1986	6.5	7.1	6.8		26 January 86	0.6	2.1	1.4
	8.6	8.8	8.7			10.2	7.8	9.0			2.1	1.9	2.0
	11.0	10.7	10.8			9.2	8.0	8.6			4.3	2.8	3.6
	12.2	13.8	13.0			6.9	6.8	6.8			4.1	2.8	3.4
	9.7	9.6	9.6			10.5	9.2	9.8			2.4	3.4	2.9
	11.1	11.9	11.5			7.2	7.2				3.3	3.4	3.4
	11.7	11.3	11.5		x_i						3.3	3.4	3.4
x_i	9.8	10.1			$x = 7.2$					x_i	4.7	3.7	4.2
$x = 10.0$											2.8	2.5	
										$x = 2.6$			

Table 2. Analysis of variance for comparisons of the methods.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F

a. Freezing calorimeter vs alcohol calorimeter.
Hypothesis: $\mu_F = \mu_A$

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Column means	$S_c = 0.6$	$c-1 = 1$	$V_c = S_c/c-1 = 0.6$	$V_c/V_e = 1.0$
Snow liquid water content, error	$S_e = 10.8$	$(c-1)(r-1) = 19$	$V_e = S_e/[(c-1)(r-1)] = 0.6$	

F_c for 1 and 19 degrees of freedom = 4.38 (95% confidence).
Since $F \le F_c$, hypothesis is accepted.

b. Dilution vs alcohol calorimeter.
Hypothesis = $\mu_D = \mu_A$

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Column means	$S_c = 0.2$	$c-1 = 1$	$V_c = S_c/c-1 = 0.2$	$V_c/V_e = 0.2$
Snow liquid water content, error	$S_e = 17.9$	$(c-1)(r-1) = 17$	$V_e = S_e/[(c-1)(r-1)] = 1.1$	

F_c (1,17) = 4.45 (95% confidence).
Since $F \le F_c$, hypothesis is accepted.

c. Capacitance meter vs alcohol calorimeter.
Hypothesis = $\mu_C = \mu_A$

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Column means	$S_c = 1.0$	$c-1 = 1$	$V_c = S_c/c-1 = 1.0$	$V_c/V_e = 1.7$
Snow liquid water content, error	$S_e = 12.5$	$(c-1)(r-1) = 20$	$V_e = S_e/[(c-1)(r-1)] = 0.6$	

F_c (1,20) = 4.35 (95% confidence).
Since $F < F_c$, hypothesis is accepted.

Definitions:

$\mu_A, \mu_C, \mu_D, \mu_F$ = population means of data for alcohol calorimeter, capacitance meter, dilution method and freezing calorimeter, respectively

c = columns of sample data

r = rows of sample data

x_{ij} = sample value at row i of column j

$\bar{x}_i$ = mean of row i of sample data

$\bar{x}_j$ = mean of column j of sample data

$\bar{x}$ = mean of all sample data

$$S_c = r \sum_{j=1}^{c} (\bar{x}_j - \bar{x})^2$$

$$S_e = r \sum_{i=1}^{r} \sum_{j=1}^{c} (x_{ij} - \bar{x}_i - \bar{x}_j + \bar{x})^2$$

F_c = critical value of F

V_c = mean square of column means

V_e = mean square of the variations in all measurements

$F = V_c/V_e$

Table 3. The 95% confidence intervals for the comparisons.

95% confidence level = 1.96 s_e

y_i = regression line value for x_i

$$s_e = \sqrt{\frac{\sum_{i=1}^{n}(y_i - y_i')^2}{n-2}}$$

	95% confidence level
Freezing vs alcohol calorimetry	±2.1 g water/100 g snow
Dilution vs alcohol calorimetry	±3.0 g water/100 g snow
Capacitance meter vs alcohol calorimetry	±2.3 cm³ water/100 cm³ snow

DISCUSSION

Which method one adopts will depend on the nature of the experiment. Both the alcohol and freezing calorimeter methods are limited to 100- to 150-g snow samples because of limits on the practical size of a field calorimeter. The dilution method can accommodate 1 to 2 L of snow without much difficulty, which makes it useful for analyzing horizontal and vertical core samples. Another advantage is that several samples can be analyzed in rapid succession by simply using more operators and insulated containers. The most useful device, however, is the capacitance meter, with which measurements can be made relatively quickly and conveniently. Large areas and liquid water depth profiles can be measured easily. The system is very compact and, other than density measurement equipment, requires no additional apparatus. Its major drawback at present is its limited availability. The liquid water content from any of the methods can be easily calculated with a programmable hand-held calculator.
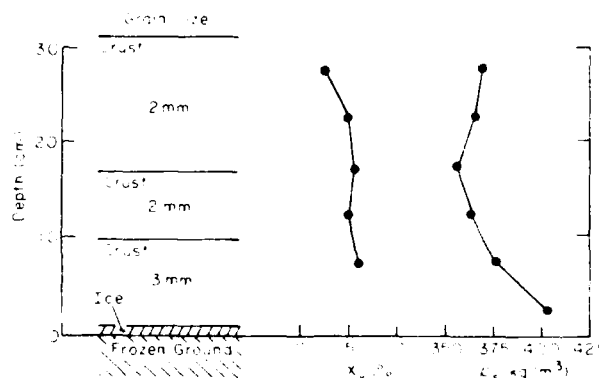

Figure 3. Snow cover profile showing stratigraphy, grain size, liquid water content and density as functions of depth. Snow grains are rounded, equilibrium growth type. Temperature of snow is uniform at 0°C.

We attempted several comparisons of each method using the natural snow cover. The maximum snow depth was 0.5 m. A typical pit profile is shown in Figure 3. The stratigraphy and spatial inhomogeneity of the snow precluded any meaningful comparison. Applying the same statistical tests as for the laboratory data consistently showed a bias in the comparisons. We attribute the bias to spatial variations in the liquid water content of the natural snow cover. This problem has been discussed previously (Denoth et al. 1984, Boyne 1985) and points out the need for environmental control of the snow when comparisons are made. Furthermore, it shows that a point measurement of liquid water content in the natural snow cover is not a reliable estimate of its spatial distribution. Variations of 10 to 15 g water/100 cm³ volume liquid water content are typical during active melting and have been studied in detail by Marsh and Woo (1984).

CONCLUSIONS

We have compared one relative and three absolute techniques for measuring the liquid water fraction of snow. We have found all of the techniques to give equivalent results. The

95% confidence interval for each comparison is compatible with the estimated errors for each method. All methods should be capable of giving acc racy of, a* worst, ± 2 g water/100 g snow or ± 1.6 g water/100 cm³ snow for a liquid water content measurement.

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The amount and distribution of liquid water in a snow cover is important for assessing its mechanical strength, meltwater generation and meltwater transmission. It also has a profound effect on the performance of active and passive remote sensing systems operating in the microwave and millimeter wave regions of the electromagnetic spectrum. New methods of measuring liquid water have been reported that show considerable promise. This report describes tests of measurement equivalence, in which are compared the three absolute methods of freezing calorimetry, alcohol calorimetry and dilution. Also compared are a calibrated capacitance snow moisture meter and one of the absolute methods. All comparisons were made in a laboratory coldroom using homogeneous snow with a mass liquid water content that varied from 0 to 14%. The comparisons show that the methods are equivalent and that the experimental errors associated with the measurements are consistent with what is expected from an error analysis of each method. However, the operational achievement of equivalence depends strongly on a variety of factors such as sample size, mixing of snow and working fluid, and operator skill.

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